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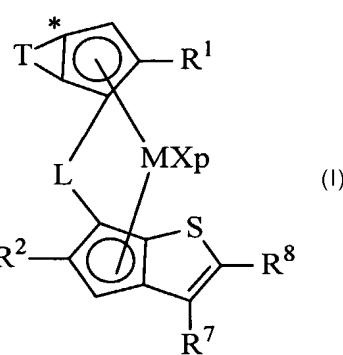
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(54) Title: PROCESS FOR POLYMERIZING 1-HEXENE OR HIGHER ALPHA-OLEFINS



(57) Abstract: A process for preparing a polymer containing derived units of one or more alpha olefins of formula $\text{CH}_2=\text{CHW}$ wherein W is a $\text{C}_3\text{-}\text{C}_{10}$ hydrocarbon radical and optionally from 0 to 81 % by mol of derived units of propylene or 1-butene, comprising contacting under polymerization conditions one or more alpha olefins of formula $\text{CH}_2=\text{CHW}$ and optionally propylene or 1-butene in the presence of a catalyst system obtainable by contacting: a) a metallocene compound of formula (I) wherein M, X, L, T, R1, R², R⁷ and R⁸ are described in the text; and (b) an alumoxane or a compound capable of forming an alkyl metallocene cation.

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Process for polymerizing 1-hexene or higher alpha-olefins

The present invention relates to a process for obtaining a polymer comprising 1-hexene or higher alpha-olefins derived units, by using a specific class of metallocene compounds, that allows to obtain polymers having high molecular weight in high yields.

Metallocene compounds are well known catalyst components for the polymerization of alpha-olefins. However they are mainly used for the (co)polymerization of ethylene, propylene and 1-butene. Polymerization of 1-hexene and higher alpha olefins by using metallocene catalyst components is discussed in some papers. For example US 6,566,544 discloses in table 10 the polymerization of 1-hexene by using $\text{Ind}_2\text{ZrMe}_2$ and bis(2-phenylindenyl)zirconium dimethyl. The molecular weight of the obtained polymers are quite low. in Macromol. Chem.Phys. 200, 1208-1219 (1999), 1-hexene is polymerized in the presence of $i\text{Pr}(\text{CpFlu})\text{ZrCl}_2$. The polymer obtained has a syndiotactic structure and the molecular mass of the polymer obtained is close to 20000 g mol^{-1} . In Journal of Polymer Science: Part A: Polymer Chemistry, Vol 37, 283-292 (1999) a series of metallocene compounds have been tested in 1-hexene polymerization. $Rac\text{-}[\text{Me}_2\text{Ge}(\eta^5\text{-C}_5\text{H}-2,3,5\text{-Me}_3)\text{MCl}_2$ ($\text{M} = \text{Zr}$ or Hf) allows to obtain 1-hexene polymers having a very high molecular weight. However the synthesis of these compounds can be difficult and the polymerization activity can be increased.

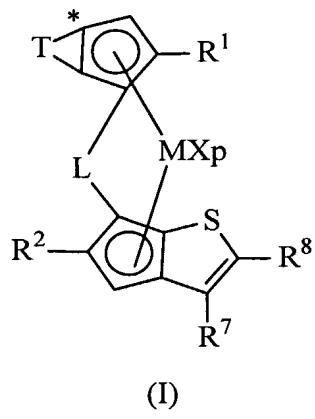
WO 01/46278 relates to a polymerization process for producing a copolymer containing from 60 to 94% mol of alpha olefins having from 3 to 6 carbon atoms, and from 6 to 40% mol of alpha olefins having at least one carbon atom more than the first one. In the examples propylene is copolymerized with 1-hexene. These copolymers are obtained with a metallocene compound different from that one used in the present invention, moreover the molecular weight of the obtained copolymers can still be improved. Finally the present invention is directed to a copolymer that contains a smaller amount of propylene or 1-butene.

Thus there is still the need to find a class of metallocene compounds able to give 1-hexene or higher alpha-olefins (co)polymers having an high molecular weight in high yields.

An object of the present invention is a process for preparing a polymer containing derived units of one or more alpha olefins of formula $\text{CH}_2=\text{CHW}$ wherein W is a $\text{C}_3\text{-C}_{10}$ hydrocarbon radical and optionally from 0 to 81% by mol; preferably from 0 to 70% by mol, more preferably from 0 to 59% by mol, of derived units of propylene or 1-butene, comprising contacting under polymerization conditions one or more alpha olefins of

formula $\text{CH}_2=\text{CHW}$ and optionally propylene or 1-butene in the presence of a catalyst system obtainable by contacting:

- a) a metallocene compound of formula (I) in the rac or racemic-like form



wherein

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements; preferably M is titanium, zirconium or hafnium;

p is an integer from 0 to 3, preferably p is 2, being equal to the formal oxidation state of the metal M minus 2;

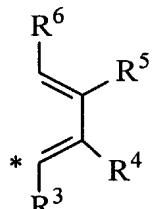
X, same or different, is a hydrogen atom, a halogen atom, or a R, OR, OSO_2CF_3 , OCOR, SR, NR₂ or PR₂ group, wherein R is a linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radicals; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R is a linear or branched C₁-C₂₀-alkyl radical; or two X can optionally form a substituted or unsubstituted butadienyl radical or a OR'O group wherein R' is a divalent radical selected from C₁-C₄₀ alkylidene, C₆-C₄₀ arylidene, C₇-C₄₀ alkylarylidene and C₇-C₄₀ arylalkylidene radicals; preferably X is a hydrogen atom, a halogen atom or a R group; more preferably X is chlorine or a C₁-C₁₀-alkyl radical; such as methyl, or ethyl radicals;

L is a divalent C₁-C₄₀ hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements or a divalent silylene radical containing up to 5 silicon atom; preferably L is a divalent bridging group selected from C₁-C₄₀ alkylidene, C₃-C₄₀ cycloalkylidene, C₆-C₄₀ arylidene, C₇-C₄₀ alkylarylidene, or C₇-C₄₀ arylalkylidene radicals optionally containing heteroatoms belonging to groups

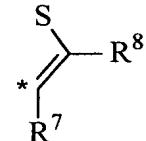
13-17 of the Periodic Table of the Elements, and silylene radical containing up to 5 silicon atoms such as SiMe₂, SiPh₂; preferably L is a group (Z(R'')₂)_n wherein Z is a carbon or a silicon atom, n is 1 or 2 and R'' is a C₁-C₂₀ hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R'' is a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably the group (Z(R'')₂)_n is Si(CH₃)₂, SiPh₂, SiPhMe, SiMe(SiMe₃), CH₂, (CH₂)₂, and C(CH₃)₂;

R¹ and R², equal to or different from each other, are C₁-C₄₀ hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably they are linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radicals; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably R¹ and R² are linear or branched, C₁-C₂₀-alkyl radicals; more preferably R¹ and R² are methyl or ethyl radicals;

T, equal to or different from each other, is a moiety of formula (IIa) or (IIb):



(IIa)



(IIb)

wherein the atom marked with the symbol * bonds the atom marked with the same symbol in the compound of formula (I);

R³ is a hydrogen atom or a C₁-C₄₀ hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R₃ is a linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-arylalkyl or a C₇-C₄₀-alkylaryl radical; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably R³ is a linear or branched, C₁-C₂₀-alkyl C₆-C₄₀-aryl, C₇-C₄₀-arylalkyl radical; even more preferably R³ is a C₆-C₂₀-aryl radical optionally substituted with one or more C₁-C₁₀ alkyl groups;

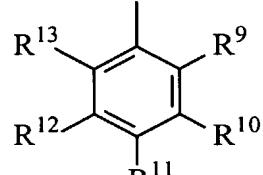
R^4 and R^6 , equal to or different from each other, are hydrogen atoms or C₁-C₄₀ hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R^4 and R^6 , equal to or different from each other, are hydrogen atoms or linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radicals; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R^4 and R^6 are hydrogen atoms;

R^5 is a hydrogen atom or a C₁-C₄₀ hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R^5 is a linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radicals; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably R^5 is a linear or branched, saturated or unsaturated C₁-C₂₀-alkyl radical; even more preferably R^5 is a methyl or ethyl radical;

R^7 and R^8 , equal to or different from each other, are hydrogen atoms or C₁-C₄₀ hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; R^7 and R^8 can optionally form a saturated or unsaturated, 5 or 6 membered rings, said ring can bear C₁-C₂₀ alkyl radicals as substituents; preferably R^7 and R^8 are hydrogen atoms or linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radicals; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

preferably R^8 is a hydrogen atom or a linear or branched, saturated or unsaturated C₁-C₂₀-alkyl radical; more preferably R^8 is a methyl or ethyl radical;

preferably R^7 is a C₁-C₄₀-alkyl, C₆-C₄₀-aryl or a C₇-C₄₀-arylalkyl; more preferably R^7 is a group of formula (III)



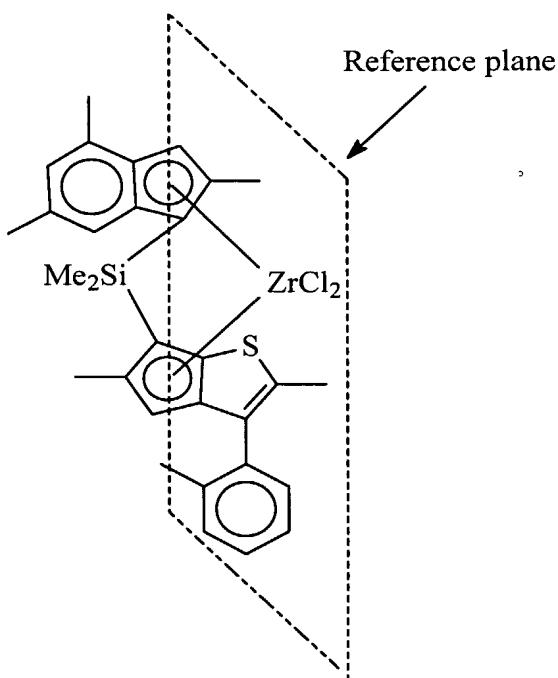
(III)

wherein R⁹, R¹⁰, R¹¹, R¹² and R¹³, equal to or different from each other, are hydrogen atoms or linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀

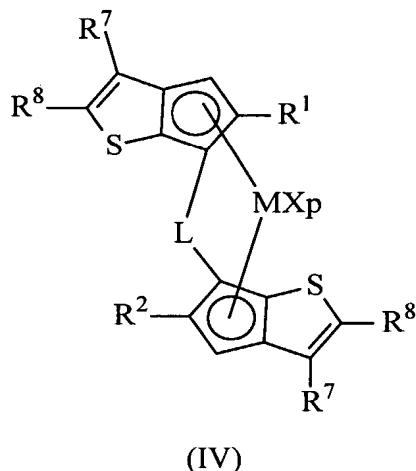
- alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R⁹, and R¹² are a hydrogen atoms; R¹⁰, R¹¹ and R¹³ are preferably hydrogen atoms or linear or branched, cyclic or acyclic, C₁-C₁₀-alkyl radicals; more preferably R¹³ and R¹⁰ are linear or branched, cyclic or acyclic, C₁-C₁₀-alkyl radicals such as methyl or ethyl radicals and R⁹, R¹¹, and R¹² are hydrogen atoms;
- b) an alumoxane or a compound capable of forming an alkyl metallocene cation; and optionally
 - c) an organo aluminum compound.

Metallocene compounds of formula (I) are well known in the art, they can be prepared according to known procedure, such as those described in WO 01/44318, WO 03/045964, PCT/EP02/13552 and DE 10324541.3.

For the purpose of the present invention the term “racemic form” means that the same substituents on the two cyclopentadienyl moieties are on the opposite side with respect to the plane containing the zirconium and the centre of the said cyclopentadienyl moieties. “racemic-like form” means that the bulkier substituents of the two cyclopentadienyl moieties on the metallocene compound are on the opposite side with respect to the plane containing the zirconium and the centre of the said cyclopentadienyl moieties as shown in the following compound:

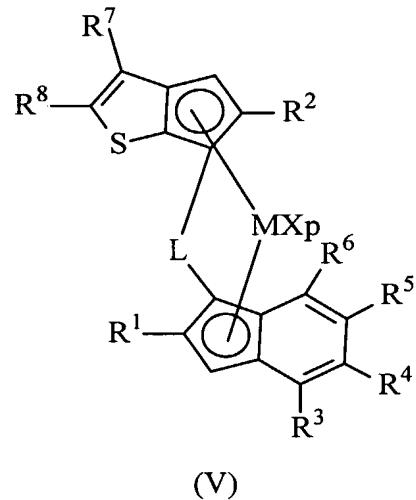


In one embodiment the compound of formula (I) has the following formula (IV)



wherein M, X, p, L, R¹, R², R⁷ and R⁸ have the above described meaning.

In an alternative embodiment the compound of formula (I) has the following formula (V)



wherein

M, X, p, L, R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ have the above described meaning.

Alumoxanes used as component b) can be obtained by reacting water with an organo-aluminium compound of formula H_jAlU_{3-j} or H_jAl₂U_{6-j}, where the U substituents, same or different, are hydrogen atoms, halogen atoms, C₁-C₂₀-alkyl, C₃-C₂₀-cyclalkyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals, optionally containing silicon or germanium atoms, with the proviso that at least one U is different from halogen, and j ranges from 0 to 1, being also a non-integer number. In this reaction the molar ratio of Al/water is preferably comprised between 1:1 and 100:1.

Alumoxanes used as component b) can be obtained by reacting water with an organo-aluminium compound of formula H_jAlU_{3-j} or H_jAl₂U_{6-j}, where the U substituents, same or different, are hydrogen atoms, halogen atoms, C₁-C₂₀-alkyl, C₃-C₂₀-cyclalkyl, C₆-C₂₀-aryl, C₇-

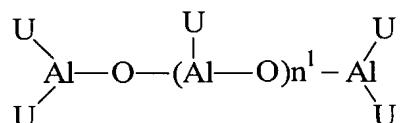
C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radicals, optionally containing silicon or germanium atoms, with the proviso that at least one U is different from halogen, and j ranges from 0 to 1, being also a non-integer number. In this reaction the molar ratio of Al/water is preferably comprised between 1:1 and 100:1.

The alumoxanes used in the process according to the invention are considered to be linear, branched or cyclic compounds containing at least one group of the type:

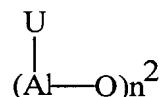


wherein the substituents U, same or different, are defined above.

In particular, alumoxanes of the formula:



can be used in the case of linear compounds, wherein n^1 is 0 or an integer of from 1 to 40 and the substituents U are defined as above; or alumoxanes of the formula:



can be used in the case of cyclic compounds, wherein n^2 is an integer from 2 to 40 and the U substituents are defined as above.

Examples of alumoxanes suitable for use according to the present invention are methylalumoxane (MAO), tetra-(isobutyl)alumoxane (TIBAO), tetra-(2,4,4-trimethylpentyl)alumoxane (TIOAO), tetra-(2,3-dimethylbutyl)alumoxane (TDMBAO) and tetra-(2,3,3-trimethylbutyl)alumoxane (TTMBAO).

Particularly interesting cocatalysts are those described in WO 99/21899 and in WO01/21674 in which the alkyl and aryl groups have specific branched patterns.

Non-limiting examples of aluminium compounds that can be reacted with water to give suitable alumoxanes (b), described in WO 99/21899 and WO01/21674, are:

tris(2,3,3-trimethyl-butyl)aluminium,	tris(2,3-dimethyl-hexyl)aluminium,	tris(2,3-dimethyl-butyl)aluminium,	tris(2-methyl-3-ethyl-hexyl)aluminium,
tris(2,3-dimethyl-pentyl)aluminium,	tris(2,3-dimethyl-heptyl)aluminium,		tris(2-methyl-3-ethyl-propyl-hexyl)aluminium,
tris(2-methyl-3-ethyl-pentyl)aluminium,			tris(2-ethyl-3-methyl-pentyl)aluminium,
tris(2-ethyl-3-methyl-butyl)aluminium,			

tris(2,3-diethyl-pentyl)aluminium, tris(2-propyl-3-methyl-butyl)aluminium, tris(2-isopropyl-3-methyl-butyl)aluminium, tris(2-isobutyl-3-methyl-pentyl)aluminium, tris(2,3,3-trimethylpentyl)aluminium, tris(2,3,3-trimethyl-hexyl)aluminium, tris(2-ethyl-3,3-dimethylbutyl)aluminium, tris(2-ethyl-3,3-dimethyl-pentyl)aluminium, tris(2-isopropyl-3,3-dimethylbutyl)aluminium, tris(2-trimethylsilyl-propyl)aluminium, tris(2-methyl-3-phenylbutyl)aluminium, tris(2-ethyl-3-phenyl-butyl)aluminium, tris(2,3-dimethyl-3-phenylbutyl)aluminium, tris(2-phenyl-propyl)aluminium, tris[2-(4-fluoro-phenyl)-propyl]aluminium, tris[2-(4-chloro-phenyl)-propyl]aluminium, tris[2-(3-isopropyl-phenyl)-propyl]aluminium, tris(2-phenyl-butyl)aluminium, tris(3-methyl-2-phenyl-butyl)aluminium, tris(2-phenyl-pentyl)aluminium, tris[2-(pentafluorophenyl)-propyl]aluminium, tris[2,2-diphenyl-ethyl]aluminium and tris[2-phenyl-2-methyl-propyl]aluminium, as well as the corresponding compounds wherein one of the hydrocarbyl groups is replaced with a hydrogen atom, and those wherein one or two of the hydrocarbyl groups are replaced with an isobutyl group.

Amongst the above aluminium compounds, trimethylaluminium (TMA), triisobutylaluminium (TIBA), tris(2,4,4-trimethyl-pentyl)aluminium (TIOA), tris(2,3-dimethylbutyl)aluminium (TDMBA) and tris(2,3,3-trimethylbutyl)aluminium (TTMBA) are preferred.

Non-limiting examples of compounds able to form an alkylmetallocene cation are compounds of formula D^+E^- , wherein D^+ is a Brønsted acid, able to donate a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and E^- is a compatible anion, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently labile to be removed by an olefinic monomer. Preferably, the anion E^- comprises one or more boron atoms. More preferably, the anion E^- is an anion of the formula $BAr_4^{(-)}$, wherein the substituents Ar which can be identical or different are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred compound, as described in WO 91/02012. Moreover, compounds of formula BAr_3 can be conveniently used. Compounds of this type are described, for example, in the International patent application WO 92/00333. Other examples of compounds able to form an alkylmetallocene cation are compounds of formula BAr_3P wherein P is a substituted or unsubstituted pyrrol radical. These compounds are described in WO01/62764. Compounds containing boron atoms can be conveniently supported according to the description of DE-A-19962814 and DE-A-19962910. All these

compounds containing boron atoms can be used in a molar ratio between boron and the metal of the metallocene comprised between about 1:1 and about 10:1; preferably 1:1 and 2:1; more preferably about 1:1.

Non limiting examples of compounds of formula D⁺E⁻ are:

Triethylammoniumtetra(phenyl)borate,

Tributylammoniumtetra(phenyl)borate,

Trimethylammoniumtetra(tolyl)borate,

Tributylammoniumtetra(tolyl)borate,

Tributylammoniumtetra(pentafluorophenyl)borate,

Tributylammoniumtetra(pentafluorophenyl)aluminate,

Tripropylammoniumtetra(dimethylphenyl)borate,

Tributylammoniumtetra(trifluoromethylphenyl)borate,

Tributylammoniumtetra(4-fluorophenyl)borate,

N,N-Dimethylbenzylammonium-tetrakis(pentafluorophenyl)borate,

N,N-Dimethylhexylammonium-tetrakis(pentafluorophenyl)borate,

N,N-Dimethylaniliniumtetra(phenyl)borate,

N,N-Diethylaniliniumtetra(phenyl)borate,

N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate,

N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)aluminate,

N,N-Dimethylbenzylammonium-tetrakis(pentafluorophenyl)borate,

N,N-Dimethylhexylammonium-tetrakis(pentafluorophenyl)borate,

Di(propyl)ammoniumtetrakis(pentafluorophenyl)borate,

Di(cyclohexyl)ammoniumtetrakis(pentafluorophenyl)borate,

Triphenylphosphoniumtetrakis(phenyl)borate,

Triethylphosphoniumtetrakis(phenyl)borate,

Diphenylphosphoniumtetrakis(phenyl)borate,

Tri(methylphenyl)phosphoniumtetrakis(phenyl)borate,

Tri(dimethylphenyl)phosphoniumtetrakis(phenyl)borate,

Triphenylcarbeniumtetrakis(pentafluorophenyl)borate,

Triphenylcarbeniumtetrakis(pentafluorophenyl)aluminate,

Triphenylcarbeniumtetrakis(phenyl)aluminate,

Ferroceniumtetrakis(pentafluorophenyl)borate,

Ferroceniumtetrakis(pentafluorophenyl)aluminate.

Triphenylcarbeniumtetrakis(pentafluorophenyl)borate, and

N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate.

Organic aluminum compounds used as compound iii) are those of formula $H_jAlU_{3,j}$ or $H_jAl_2U_{6-j}$ as described above.

The polymerization process of the present invention can be carried out in liquid phase, optionally in the presence of an inert hydrocarbon solvent. Said hydrocarbon solvent can be either aromatic (such as toluene) or aliphatic (such as propane, hexane, heptane, isobutane, cyclohexane and 2,2,4-trimethylpentane). Preferably, the polymerization process of the present invention is carried out by using the alpha olefin of formula $CH_2=CHW$ wherein W is a C_3-C_{10} hydrocarbon radical such as 1-hexene or 1-octene as polymerization medium, i.e. the same olefin that is going to be polymerized for example 1-hexene is used as polymerization medium when a 1-hexene based polymer is the wished polymer.

The polymerization temperature preferably ranges from 0°C to 250°C; preferably comprised between 20°C and 150°C and, more particularly between 40°C and 90°C;

The molecular weight distribution can be varied by using mixtures of different metallocene compounds or by carrying out the polymerization in several stages which differ as to the polymerization temperature and/or the concentrations of the molecular weight regulators and/or the monomers concentration. Moreover by carrying out the polymerization process by using a combination of two different metallocene compounds of formula (I) a polymer endowed with a broad melting is produced.

With the process of the present invention isotactic polymers endowed with high molecular weights can be obtained in high yields.

With the process of the present invention polymers containing derived units of one or more alpha olefins of formula $CH_2=CHW$ wherein W is a C_3-C_{10} hydrocarbon radical and optionally from 0 to 81% by mol of derived units of propylene or 1-butene can be obtained. Examples of alpha olefins of formula $CH_2=CHW$ are 1-pentene; 1-hexene; 1-octene and 1-decene. Preferably 1-hexene and 1-octene are used; more preferably 1-hexene is used.

When said alpha olefins of formula $CH_2=CHW$ are copolymerized with propylene or 1-butene preferably the obtained copolymer has a content of derived units of propylene or 1-butene ranging from 0.1% by mol to 59% by mol; more preferably the content of propylene or 1-butene ranges from 10% by mol to 50% by mol, even more preferably it ranges from 19% by mol to 40% by mol.

The obtained copolymer is endowed with the following properties:

- i) intrinsic viscosity IV measured in tetrahydronaphthalene (THN) at 135°C higher than 0.90 dl/g; preferably higher than 1.20 dl/g; more preferably higher than 1.30 dl/g; even more preferably higher than 1.80 dl/g;
- ii) distribution of molecular weight Mw/Mn lower than 3; preferably lower than 2.5; and
- iii) no enthalpy of fusion detectable at a differential scanning calorimeter (DSC) wherein the DSC measurement is carried out as described below.

In said copolymer the alpha olefin of formula $\text{CH}_2=\text{CHW}$ is preferably 1-hexene and 1-octene.

The copolymers, other than the above properties, are further endowed with a very low Shore A (measured according to ISO 868), in particular the shore A is lower than 30; preferably lower than 25; more preferably lower than 20; and furthermore the tensile modulus is lower than 20 MPa (measured according to ASTM 5026,4092 e 4065); preferably lower than 15MPa; more preferably lower than 11 MPa.

A further preferred range of content of derived units of propylene and 1-butene is from 19% by mol to 59% by mol; even more preferably from 30% by mol to 59% by mol.

The process of the present invention is particularly suitable for preparing homopolymers of alpha olefins of formula $\text{CH}_2=\text{CHW}$ wherein W is a $\text{C}_3\text{-}\text{C}_{10}$ hydrocarbon radical, in particular homopolymers of 1-hexene or 1-octene; preferably homopolymer of 1-hexene are produced.

The homopolymer prepared according to the present invention can be used for application known in the art such as masterbatches or in adhesive formulations.

Even if the homopolymer of the present invention are not exemplified, their preparation can be easily achieved by the skilled man once it is known the process for preparing the copolymers. In fact it is sufficient to avoid to add the comonomer in the processes exemplified above for obtaining the wished homopolymer.

The copolymers obtainable with the process of the present invention described above, can have the same uses of the homopolymer and furthermore they can be used as compatibilizer. For example they can improve the dispersion of a rubber phase in an crystalline matrix, due to the presence of the comonomer that help to compatibilize the two phases, so that a material having an improved izod impact value can be obtained.

The following examples are given to illustrate and not to limit the invention.

EXAMPLES

GENERAL PROCEDURES AND CHARACTERIZATIONS

All chemicals were handled under nitrogen using standard Schlenk techniques.

Methylalumoxane (MAO) was received from Albemarle as a 30% wt/vol toluene solution and used as such.

Pure triisobutylaluminum (TIBA) was used as such.

Isododecane was purified over aluminum oxide to reach a water content below 10 ppm.

A 101 g/L TIBA/isododecane solution was obtained by mixing the above components.

The melting points of the polymers (T_m) were measured by Differential Scanning Calorimetry (D.S.C.) on a Perkin Elmer DSC-7 instrument, according to the standard method. A weighted sample (5-7 mg) obtained from the polymerization was sealed into aluminum pans and heated to 180°C at 10°C/minute. The sample was kept at 180°C for 5 minutes to allow a complete melting of all the crystallites, then cooled to 20°C at 10°C/minute. After standing 2 minutes at 20°C, the sample was heated for the second time to 180°C at 10°C/min. In this second heating run, the peak temperature was taken as the melting temperature (T_m) and the area of the peak as melting enthalpy (ΔH_f).

Molecular weight parameters were measured using a Waters 150C ALC/GPC instrument (Waters, Milford, Massachusetts, USA) equipped with four mixed-gel columns PLgel 20 μm Mixed-A LS (Polymer Laboratories, Church Stretton, United Kingdom). The dimensions of the columns were 300 \times 7.8 mm. The solvent used was TCB and the flow rate was kept at 1.0 mL/min. Solution concentrations were 0.1 g/dL in 1,2,4 trichlorobenzene (TCB). 0.1 g/L of 2,6-di-t-butyl-4-methyl phenol (BHT) was added to prevent degradation and the injection volume was 300 μL . All the measurements were carried out at 135°C. GPC calibration is complex, as no well-characterized narrow molecular weight distribution standard reference materials are available for 1-hexene polymers. Thus, a universal calibration curve was obtained using 12 polystyrene standard samples with molecular weights ranging from 580 to 13,200,000. It was assumed that the K values of the Mark-Houwink relationship were: $K_{PS} = 1.21 \times 10^{-4}$, dL/g and $K_{PH} = 1.78 \times 10^{-4}$ dL/g for polystyrene and poly-1-hexene respectively, for the copolymers the same K_{PH} has been used. The Mark-Houwink exponents α were assumed to be 0.706 for polystyrene and 0.725 for poly-1-hexene and copolymers. Even though, in this approach, the molecular parameters obtained were only an estimate of the hydrodynamic volume of each chain, they allowed a relative comparison to be made.

The intrinsic viscosity (I.V.) was measured in tetrahydronaphthalene (THN) at 135°C.

rac-dimethylsilandiylbis-6-[2,5-dimethyl-3-(2'-methyl-phenyl)cyclopentadienyl-[1,2-b]-thiophene]zirconium dichloride (A-1) was prepared according to WO01/44318.

Preparation of catalyst systems

Preparation of catalyst system C-1 A-1/MAO:TIBA 2:1 (400)

9.8cc of TIBA/isododecane solution (101g/L) were mixed with 1.91 cc of MAO/ toluene solution (Albemarle -30%wt) to obtain a MAO/TIBA molar ratio of 2:1. The solution was stirred for 1 hour at room temperature. Then, 26 mg of A-1 were dissolved in the solution. The orange solution did not show any trace of residual solid .

The final solution was diluted with 4 cc of isododecane to reach a concentration of 100g/L.

Polymerization tests

1-hexene copolymerisation

An amount of purified liquid 1-hexene as indicated in table 1 was transferred reactor at room temperature in a 250 glass vessel under nitrogen atmosphere. The reactor had been maintained under slight positive nitrogen atmosphere at all time. Consequently the temperature was increased to the polymerization temperature indicated in table 2 and an over pressure of 1 bar-g of propylene or 1-butene was fed in the autoclave. The catalyst solution, (ageing indicated in table 2), was fed into the liquid, under a nitrogen flow. The pressure was increased adding propylene until reaching the polymerisation pressure indicated in table 2. The polymerization was conducted for 60 minutes, then stopped by flashing the monomers. The polymer was precipitated by adding acetone to the polymer solution. The recovered polymer was dried at 50°C under vacuum. Polymerization and polymer data are reported in table 1.

Table 1

Ex	Cat (mg. of A-1)	1-hexene g	Monomer (bar-g)	Pol. Temp. °C	Ageing hours	Activity Kg/g met/h
1	C-1 (1.3)	54	propylene (3)	50	48	20
2	C-1 (1)	54	propylene (6)	50	144	12
3	C-1 (1.64)	54	1-butene (2)	70	216	27
4	C-1 (1.64)	54	1-butene (2)	50	24	22

Table 1 continued

Ex	1-hexene mol%	Mw	Mw/Mn	IV (THN) dl/g	ΔH
1	79.1	223700	1.9	1.21	n.d.
2	63.7	286500	2.1	1.6	n.d.
3	75.4	n.a.	n.a.	n.a.	n.d.
4	62.3	n.a.	n.a.	n.a.	n.d.

n.a. not available

n.d. not detectable.

1-hexene/propylene copolymerisation

4 mmol of Al(*i*-Bu)₃ (as a 1M solution in hexane) and 1000g of 1-hexene were charged at room temperature in a 4-L jacketed stainless-steel autoclave, previously purified by washing with an Al(*i*-Bu)₃ solution in hexane and dried at 50°C in a stream of nitrogen. The autoclave was then thermostated at the polymerisation temperature, 70°C, and then the solution containing the catalyst/cocatalyst solution indicated in table 3 prepared 12 hours before was injected in the autoclave by means of nitrogen pressure through the stainless-steel vial. The monomer was fed until a pressure indicated in table 3 and the polymerisation carried out at constant temperature for 1 hour. The pressure into the autoclave is decreased until 20 bar-g and the polymerization solution is discharged into a heated steel tank containing water at 70°C. The tank heating is switched off and a flow of nitrogen at 0.5 bar-g is fed. After cooling at room temperature, the steel tank is opened and the wet polymer collected and dried at 70°C under reduced pressure. The polymerisation conditions and the characterisation data of the obtained polymers are reported in Table 2.

table 2

Ex	Cat (mg. of met)	Monomer bar-g	Activity Kg/g met/ h	1-hexene mol%	Mw	Mw/Mn	IV (THN) dl/g	ΔH
5	C-1 (6.56)	propylene (19)	53	26	184500	2	1.2	n.a.
6	C-1 (6.56)	propylene (13)	23	42	172100	2	1.0	n.d.
7	C-1 (6.56)	1-butene (5)	24	43	177700	2	1.0	n.d.

n.a. not available

n.d. not detectable.

The shore A (ISO 868) of copolymers of examples 6 and 7 has been measured, the results are reported in table 3. The tensile modulus of a sample of copolymers obtained in examples 6 and 7 has been measured according to ASTM 5026,4092 and 4065 as follows: Specimens for tensile test are cut from compression moulding plaques. Specimen sizes are approx. 40 mm long overall, 20 mm inter-clamp length, 6 mm width and thickness was 1 mm. Specimen is clamped in the SEIKO DMS 6100 tensile DMTA.

The applied frequency is 1 Hz.

Specimens are heated from -80°C to +140°C with 2°C/min as heating rate; specimens are re-clamped at the low temperature.

The results are reported in table 3

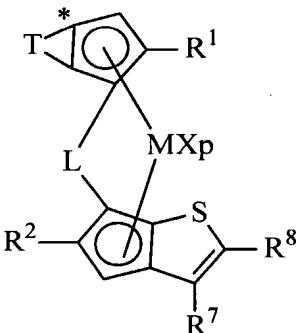
Table 3

Ex	shore A	tensile modulus (MPa)
6	5	<10
7	4	<10

Claims

1. A process for preparing a polymer containing derived units of one or more alpha olefins of formula $\text{CH}_2=\text{CHW}$ wherein W is a C₃-C₁₀ hydrocarbon radical and optionally from 0 to 81% by mol of derived units of propylene or 1-butene, comprising contacting under polymerization conditions one or more alpha olefins of formula $\text{CH}_2=\text{CHW}$ and optionally propylene or 1-butene in the presence of a catalyst system obtainable by contacting:

- a) a metallocene compound of formula (I)



(I)

wherein

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements;

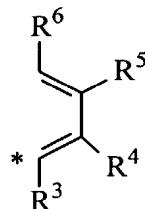
p is an integer from 0 to 3, being equal to the formal oxidation state of the metal M minus 2;

X, same or different, is a hydrogen atom, a halogen atom, or a R, OR, OSO₂CF₃, OCOR, SR, NR₂ or PR₂ group, wherein R is a linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radicals; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two X can optionally form a substituted or unsubstituted butadienyl radical or a OR'O group wherein R' is a divalent radical selected from C₁-C₄₀ alkylidene, C₆-C₄₀ arylidene, C₇-C₄₀ alkylarylidene and C₇-C₄₀ arylalkylidene radicals;

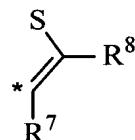
L is a divalent C₁-C₄₀ hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements or a divalent silylene radical containing up to 5 silicon atom;

R¹ and R², equal to or different from each other, are C₁-C₄₀ hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

T, equal to or different from each other, is a moiety of formula (IIa) or (IIb):



(IIa)



(IIb)

wherein the atom marked with the symbol * bonds the atom marked with the same symbol in the compound of formula (I);

R³ is a hydrogen atom or a C₁-C₄₀ hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

R⁴ and R⁶, equal to or different from each other, are hydrogen atoms or C₁-C₄₀ hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

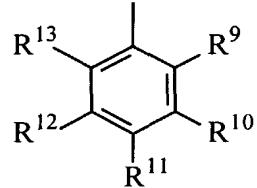
R⁵ is a hydrogen atom or a C₁-C₄₀ hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

R⁷ and R⁸, equal to or different from each other, are hydrogen atoms or C₁-C₄₀ hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; R⁷ and R⁸ can optionally form a saturated or unsaturated, 5 or 6 membered rings, said ring can bear C₁-C₂₀ alkyl radicals as substituents; and

- (b) an alumoxane or a compound capable of forming an alkyl metallocene cation;
- 2. The process according to claim 1 wherein the catalyst system further contains c) an organo aluminum compound.
- 3. The process according to claims 1 or 2 wherein in the compound of formula (I) M is titanium, zirconium or hafnium; X is a hydrogen atom, a halogen atom or a R

group, wherein R has been defined as in claim 1; and L is a divalent bridging group selected from C₁-C₄₀ alkylidene, C₃-C₄₀ cycloalkylidene, C₆-C₄₀ arylidene, C₇-C₄₀ alkylarylidene, or C₇-C₄₀ arylalkylidene radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and silylene radical containing up to 5 silicon atoms.

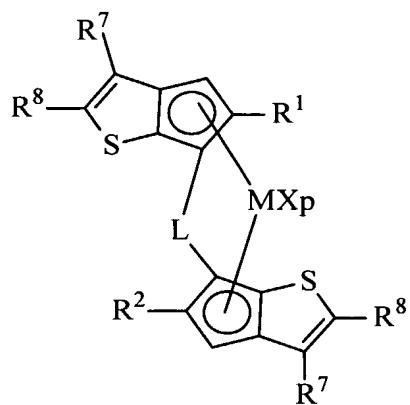
4. The process according to anyone of claims 1-3 wherein in the compound of formula (I) L is a group (Z(R'')_n) where Z is a carbon or a silicon atom, n is 1 or 2 and R'' is a C₁-C₂₀ hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements.
5. The process according to anyone of claims 1-4 wherein R¹ and R² are linear or branched, saturated or unsaturated C₁-C₂₀-alkyl radicals; R³ is a linear or branched, C₁-C₂₀-alkyl C₆-C₄₀-aryl, C₇-C₄₀-arylalkyl radical; R⁴ and R⁶ are hydrogen atoms; R⁵ is a linear or branched, saturated or unsaturated C₁-C₂₀-alkyl radical; R⁸ is a hydrogen atom or a linear or branched, saturated or unsaturated C₁-C₂₀-alkyl radical; and R⁷ is a C₁-C₄₀-alkyl, C₆-C₄₀-aryl or a C₇-C₄₀-arylalkyl radical.
6. The process according to claim 5 wherein R⁷ is a group of formula (III)



(III)

wherein R⁹, R¹⁰, R¹¹, R¹² and R¹³, equal to or different from each other, are hydrogen atoms or linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements.

7. The process according to anyone of claims 1-6 wherein the metallocene compound has formula (IV):

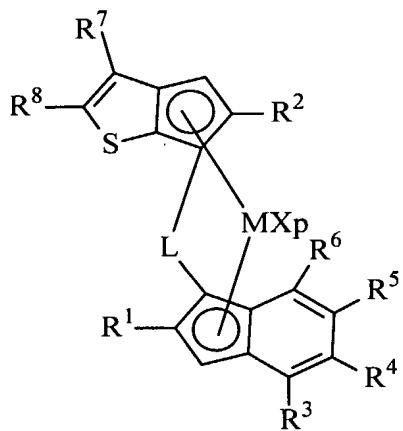


(IV)

wherein

M, X, p, L, R¹, R², R³, R⁴, R⁵ and R⁶ have the meaning described in claim 1.

8. The process according to anyone of claims 1-6 wherein the metallocene compound in its meso or meso-like form has formula (V):



(V)

wherein M, X, p, L, R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ have the meaning described in claim 1.

9. The process according to anyone of claims 1-7 wherein the polymerization process is carried out by using 1-hexene as polymerization medium.
10. The process according to anyone of claims 1-8 wherein 1-hexene is homopolymerized.
11. The process according to anyone of claims 1-8 wherein 1-hexene is copolymerized with propylene or 1-butene.

12. A copolymer comprising from 41% by mol to 99.9% by mol of derived units of alpha olefins of formula $\text{CH}_2=\text{CHW}$ wherein W is a C₃-C₁₀ hydrocarbon radical and from 0.1 to 59% by mol of derived units of propylene or 1-butene endowed with the following properties:
 - i) intrinsic viscosity IV measured tetrahydronaphthalene (THN) at 135°C higher than 0.9 dl/g;
 - ii) distribution of molecular weight Mw/Mn lower than 3; preferably lower than 2.5; and
 - iii) no enthalpy of fusion detectable at a differential scanning calorimeter (DSC).
13. A copolymer according to claim 11 endowed with a shore A lower than 30 and a tensile modulus lower than 20 MPa.
14. A blend comprising the copolymer of claims 11 or 12.
15. Use of the copolymer of claims 11 and 12 as compatibilizer in an heterophasic blend comprising a crystalline matrix and a rubber phase.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/002480

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F210/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/44318 A (BASELL TECHNOLOGY COMPANY B.V; EWEN, JOHN, A; ELDER, MICHAEL, J; JONES) 21 June 2001 (2001-06-21) cited in the application the whole document -----	1-11
X	EP 1 327 636 A (BASELL POLYOLEFINE GMBH) 16 July 2003 (2003-07-16) page 19, paragraph 112; examples 4,5,15,16 -----	1-11
X	WO 03/045964 A (BASELL POLYOLEFINE GMBH; ELDER, MICHAEL, J; JONES, ROBERT, L., JR) 5 June 2003 (2003-06-05) claim 6; examples 1-5 ----- -/--	1-11

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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- "&" document member of the same patent family

Date of the actual completion of the international search

2 June 2005

Date of mailing of the international search report

10/06/2005

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/002480

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 2004/050713 A (BASELL POLYOLEFINE GMBH; RESCONI, LUIGI; PELLICONI, ANTEO; GARAGNANI,) 17 June 2004 (2004-06-17) examples 1-4 -----	1-11
X	EP 0 604 908 A (BASELL TECHNOLOGY COMPANY B.V; SPHERILENE S.R.L) 6 July 1994 (1994-07-06) example 20 -----	12-15
X	GB 999 725 A (EASTMAN KODAK COMPANY) 28 July 1965 (1965-07-28) the whole document -----	12-15
X	US 6 232 421 B1 (FUJITA MASAYUKI ET AL) 15 May 2001 (2001-05-15) the whole document -----	12-15
X	THOMANN R ET AL: "Crystallisation of syndiotactic poly(propene-co-octene)" POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 39, no. 10, May 1998 (1998-05), pages 1907-1915, XP004108236 ISSN: 0032-3861 the whole document -----	12-15
X	TOSHIHIKO SUGANO ET AL: "EFFECT OF CATALYST ISOSPECIFICITY ON THE COPOLYMERIZATION OF PROPENE WITH 1-HEXENE" MAKROMOLEKULARE CHEMIE, MACROMOLECULAR CHEMISTRY AND PHYSICS, HUTHIG UND WEPF VERLAG, BASEL, CH, vol. 193, no. 1, January 1992 (1992-01), pages 43-51, XP000259411 ISSN: 0025-116X the whole document -----	12-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2005/002480

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 0144318	A	21-06-2001	US	6444833 B1	03-09-2002
			AU	778205 B2	25-11-2004
			AU	3007901 A	25-06-2001
			BR	0010043 A	22-01-2002
			CA	2362093 A1	21-06-2001
			CN	1347424 A ,C	01-05-2002
			WO	0144318 A1	21-06-2001
			EP	1153047 A1	14-11-2001
			JP	2003517010 T	20-05-2003
			PL	349318 A1	15-07-2002
			US	6635779 B1	21-10-2003
			ZA	200106367 A	04-11-2002
EP 1327636	A	16-07-2003	EP	0938491 A1	01-09-1999
			EP	1327636 A2	16-07-2003
			AU	733813 B2	24-05-2001
			AU	5321698 A	10-06-1998
			BR	9715006 A	05-12-2000
			CA	2271861 A1	28-05-1998
			CN	1244201 A ,C	09-02-2000
			DE	69721807 D1	12-06-2003
			DE	69721807 T2	04-03-2004
			WO	9822486 A1	28-05-1998
			ES	2197377 T3	01-01-2004
			HU	9904527 A2	28-05-2000
			ID	22443 A	14-10-1999
			JP	2001504824 T	10-04-2001
			KR	2000053294 A	25-08-2000
			NO	992352 A	08-07-1999
			PL	333462 A1	20-12-1999
			RU	2194708 C2	20-12-2002
			TR	9901635 T2	21-02-2000
			TW	394779 B	21-06-2000
			ZA	9710211 A	03-06-1998
WO 03045964	A	05-06-2003	WO	03045964 A1	05-06-2003
			EP	1448578 A1	25-08-2004
			JP	2005510567 T	21-04-2005
			US	2005010058 A1	13-01-2005
WO 2004050713	A	17-06-2004	AU	2003296585 A1	23-06-2004
			WO	2004050713 A2	17-06-2004
EP 0604908	A	06-07-1994	IT	1256259 B	29-11-1995
			CA	2112598 A1	01-07-1994
			DE	69330780 D1	25-10-2001
			DE	69330780 T2	04-07-2002
			EP	0604908 A2	06-07-1994
			ES	2162802 T3	16-01-2002
			FI	935913 A	01-07-1994
			JP	6256369 A	13-09-1994
			RU	2169152 C2	20-06-2001
GB 999725	A	28-07-1965	FR	1296956 A	22-06-1962
US 6232421	B1	15-05-2001	JP	3533923 B2	07-06-2004
			JP	11209428 A	03-08-1999
			CN	1229096 A ,C	22-09-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP2005/002480

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 6232421	B1	DE US	19902814 A1 2001009953 A1	29-07-1999 26-07-2001